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Structural characterization of nanoscale intermetallic precipitates in highly neutron irradiated reactor pressure vessel steels

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ABSTRACT

Massive, thick-walled pressure vessels are permanent nuclear reactor structures that are exposed to a damaging flux of neutrons from the adjacent core. The neutrons cause embrittlement of the vessel steel that grows with dose (fluence), as manifested by an increasing ductile-to-brittle fracture transition temperature. Extending reactor life requires demonstrating that large safety margins against brittle fracture are maintained at the higher neutron fluence associated with beyond 60 years of service. Here synchrotron-based x-ray diffraction and small angle x-ray scattering measurements are used to characterize highly embrittling nm-scale Mn–Ni–Si precipitates that develop in the irradiated steels at high fluence. These precipitates lead to severe embrittlement that is not accounted for in current regulatory models. Application of the complementary techniques has, for the very first time, successfully identified the crystal structures of the nanoprecipitates, while also yielding self-consistent compositions, volume fractions and size distributions.

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1. Introduction

Reactor pressure vessels (RPVs) are the primary permanent component of light water reactors (LWRs). RPVs experience irradiation embrittlement that increases with neutron fluence (see Refs [1–3] for overviews of the embrittlement phenomena and underlying mechanisms). Ensuring that large safety margins are maintained in the face of embrittlement is required to extend LWR service life to beyond 60 years. Embrittlement is marked by increases in the ductile-to-brittle transition fracture temperature (ΔT) of RPV steels. The ΔT is primarily caused by irradiation hardening ($\Delta\sigma_y$) associated with the formation of nm-scale precipitates and solute–defect complexes that act as obstacles to dislocation glide. At low to intermediate neutron fluence, significant hardening and embrittlement is primarily caused by the formation of coherent, transition phase copper rich precipitates (CRP). Trace impurity amounts of Cu (<0.35 at.%) are insoluble in steels and rapidly phase separate due to radiation enhanced diffusion (RED) at RPV service temperatures (around 290 °C). RED is due to excess concentrations of vacancies produced by neutron displacement damage. The CRPs are also enriched in Mn, Ni and Si, in the form of a core (primarily Cu)–shell (primarily Mn–Ni–Si) structure. The hardening and embrittlement due to CRPs saturate when the Cu is depleted from the ferrite matrix. However, the Mn, Ni and Si solutes continue to slowly accumulate in

the precipitates, that grow to large volume fractions (up to ~3%) at high fluence since there is much more Mn + Ni + Si (e.g. >2.5%) than Cu in typical low alloy RPV steels. Further, it was long ago predicted [4–6], and more recently shown [7–11] that Mn–Ni–Si precipitates (MNSPs) can also form in low or Cu free steels, but only at sufficiently high fluence. Hence the MNSPs have also been called late blooming phases. The ΔT approximately scales as $300\text{ °C} \times \sqrt{f}$, where f is the volume fraction of the precipitates [1,2,10]. Thus the large volume fractions associated with MNSP could limit safe extended RPV lifetimes. However, late blooming MNSPs are not accounted for in current embrittlement regulatory models based on lower fluence databases.

Solute precipitation and embrittlement are complex phenomenon that depend on the combination of both metallurgical (microstructure, composition, product form and heat treatment) and irradiation (neutron flux, fluence, irradiation temperature) variables. RPV steels have a very wide range of compositions that may be vulnerable to MNSP: Cu = 0.02–0.35, Mn = 0.8–1.6, Ni = 0.2–1.6, Si = 0.4–1.2 in at.%. Formation of MNSP also depends on the irradiation temperature, flux and fluence. In general, MNSPs are promoted by higher Ni and Cu, lower temperatures and flux and, as noted previously, high fluence. Thus there is a pressing need to incorporate MNSP effects into embrittlement models that can reliably extrapolate ΔT predictions to extended life at high-fluence, low-flux service conditions, where little or no data currently exists. This requires robust physical models that are informed and calibrated by well-designed experiments and characterization studies.

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The radiation-induced precipitation in RPV steels has primarily been studied by small angle neutron scattering (SANS) and atom probe tomography (APT). The APT studies provide good measures of CRP and MNSP number densities (N), volume fractions (f), size distributions and average sizes (d) and show that their compositions lie in the vicinity of the G ($Mn_6Ni_{16}Si_7$) and Γ_2 (Mn_2Ni_3Si) phases in the Mn–Ni–Si ternary projection of the Fe-based quaternary system phase diagram at around 290 °C [10,12]. However, neither SANS nor APT provides information on the crystal structure of the MNSP. Phase identification is needed to develop rigorous thermodynamic and kinetic precipitation models. However, characterizing MNSP crystal structures is very difficult, due to their nm-scale sizes, complex chemistry and limited volume fractions [9,13]. In principle, transmission electron microscopy (TEM) can be used for structure identification, but this has had limited success, indexing the G -phase in only a few cases. Of course, the basic thermodynamics of phase formation can be used to predict the phase selection. Notably, Thermocalc enabled Calphad models predict G and Γ_2 phases in the RPV steel region of the Fe–Mn–Ni–Si quaternary phase diagram, with mole fractions and compositions that are reasonably consistent with the APT measurements [10,11].

Standard x-ray diffraction techniques suffer many of the same challenges to phase identification [14,15]. However, in this work, advanced synchrotron x-ray techniques were used to successfully identify the dominant MNSP intermetallic phases in a set of six irradiated RPV steels with systematic variations in Cu and Ni contents. Phase identification was enabled by a combination of small angle x-ray scattering (SAXS) and x-ray diffraction (XRD). The corresponding results of the synchrotron x-ray techniques for MNSP f and d are shown to be internally self-consistent and in good agreement with APT measurements and thermodynamic predictions.

2. Materials and methods

The chemical compositions of the six split melt RPV steels investigated are shown in Table 1. The L-series alloy includes increasing amounts of Cu (LG, LH, LI and LC) and intermediated and higher contents of Ni (LC and LD). The CM6 alloy is nearly Cu free, but contains a large amount of Ni. Specimens in the form of 2×0.5 mm discs were wrapped in three layers of Kapton to prevent any radioactive contamination at the synchrotron beamline. The alloys were previously irradiated to a high-fluence of $\sim 1.10 \times 10^{21}$ n/cm² at 290 °C in the Idaho National Laboratory Advanced Test Reactor (ATR) at a neutron flux of $\sim 2.3 \times 10^{14}$ n/cm²-s.

High-resolution XRD measurements were performed at the National Synchrotron Light Source using the high-energy x-rays available at beamline X17A. SAXS measurements were performed at the X-ray Powder Diffraction (XPD) beamline of the new National Synchrotron Light Source-II. All measurements were performed in transmission mode with an amorphous silicon-based flat panel detector (Perkin-Elmer) mounted orthogonal to and centered on the beam path. The sample-to-detector distances and tilts of the detector relative to the beam were refined using either CeO₂ (XRD), or Silver Behenate (SAXS) powder standards. The wavelengths of the incident x-rays were 0.1839 Å (67.42 keV, X17A) and 0.2361 Å (52.51 keV, XPD). The sample-to-detector distances were calculated to be 780 mm for XRD (with maximum two theta ranges of 20°) and 2893 mm for SAXS

(with a Q -range of 0.01–0.8 Å⁻¹). Multiple patterns were collected to avoid saturation of the detector. Typical count times were 0.5–1 s (depending on the sample). Each diffraction or scattering pattern consisted of the average of 100–500 individual exposures. All raw two-dimensional patterns were background corrected by subtracting the dark current image and Kapton/air scattering. Noticeable artifacts in the images (like the beam stop or dead pixels) were masked. The corrected and masked two-dimensional detector images were then averaged and radially integrated to obtain the one-dimensional powder diffraction and SAXS patterns.

The measured SAXS intensities were converted to absolute cross-section units following the methods described in Ref [16]. Precipitate sizes were determined using the nonlinear least square fitting procedures in the IGOR Pro-based software package IRENA [17]. Spherical particles were assumed, consistent with previous APT and TEM measurements [10]. The electron density difference (or atomic density difference) between the matrix and the precipitates were calculated within IRENA based on their respective bulk-phase values.

The Kapton/air background subtracted XRD patterns were Rietveld refined with the TOPAS software package (BRUKER). The peak profiles were modeled by a modified pseudo-Voigt function. The instrument contribution to the broadening of the measured profiles was quantified by fitting a CeO₂ NIST powder standard (38 hkl reflections), with known crystalline-domain size and negligible strain contribution. The Gaussian and Lorentzian-based broadening parameters were subsequently fixed during the analysis of the alloys under investigation. The volume fraction f , domain size, lattice parameter, and strain were allowed to vary during the Rietveld refinements, with the isotropic temperature factors [18] nominally fixed to their bulk values taken from the literature [13,16,19–21]. The strain components for the small austenite fcc phase [22], the cementite (alloyed Fe₃C type phase) and MNSPs (described below) were not included in the refinements due to the known complications to their quantification at such small sizes [23, 24]. Therefore, the refined size parameters of the cementite and austenite phases are lower limits. Furthermore, in the case of the irradiated alloys, where the diffraction contributions of the nm-scale MNSP are small, the precipitate size, determined from SAXS, was fixed and only f and the lattice parameter were allowed to vary during the refinement. This method is similar to that employed in the field of mineralogy to determine the structure and fraction of a phase with partial or no known crystal structure (PONKCS) [25,26].

3. Results and discussion

3.1. Small-angle x-ray scattering

Fig. 1 shows the background corrected SAXS patterns for the (a) LD and (b) CM6-unirradiated and irradiated alloys (alloys with the highest and lowest Cu content, respectively). The scattering intensity at low- Q , is indicative of features with sizes of ~ 40 –70 nm, that can be attributed to the cementite particles. The SAXS patterns for all the alloys were found to change significantly following irradiation. The increase in the scattering amplitude at higher Q in the irradiated samples is due to the formation of new nm-scale MNSP that are remarkably quantitatively consistent with APT measurements [10]. Table 2 summarizes the SAXS and APT d and f .

3.2. X-ray diffraction

Fig. 2 shows XRD patterns for (a) LD and (b) LG unirradiated and irradiated alloys with the identified phases superimposed for reference. The quantitative Rietveld results (see supplementary information) for the unirradiated samples show that the line broadening from the strain components are small for the ferrite phase. All the unirradiated alloys also display a Fe₃C contribution ($f = 2.1$ –2.7%) and a small fcc phase contribution ($f = 0.6$ –1.8%). These small fcc crystallites are primarily

Table 1
Nominal chemical compositions (wt.%) for the RPV samples.

Sample ID	Cu	Ni	Mn	Mo	P	C	Si	Fe + imp
LC	0.41	0.86	1.44	0.55	0.005	0.14	0.23	balance
LD	0.38	1.25	1.38	0.55	0.005	0.19	0.23	balance
LG	0.01	0.74	1.37	0.55	0.005	0.16	0.22	balance
LH	0.11	0.74	1.39	0.55	0.005	0.16	0.24	balance
LI	0.2	0.74	1.37	0.55	0.005	0.16	0.24	balance
CM6	0.02	1.68	1.5	0.54	0.007	0.15	0.17	balance

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